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Relationships Involving Fine Particle Mass Fine Particle Sulfur and Ozone during Episodic Periods at Sites in and Around St. Louis, Missouri

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16. ABSTRACT

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RELATIONSHIPS INVOLVING FINE PARTICLE MASS, FINE PARTICLE SULFUR AND OZONE DURING EPISODIC PERIODS AT SITES IN AND AROUND ST. LOUIS, MO

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Abstract—The measurements during episodic periods in the St. Louis area in 1975 and 1976 of fine particle sulfur, fine particle mass and ozone are related. Such episodes are concentrated into time periods in the late spring and summer months. During such episodes, particle sulfur is the major constituent of the fine particle mass. The sum of the non-sulfur species in the fine particle mass do not show similar episodic patterns as the fine particle sulfur.

Elevated concentrations of fine particle sulfur and of ozone usually occur together within the same episodic time periods. However, the day to day variations in fine particle sulfur and of ozone do differ somewhat within these time periods.

Both fine particle sulfur and ozone show the influence of regional scale and local scale atmospheric photochemical processes on their formation during episodic time periods. Regional scale boundary layer processes frequently appear to contribute more to fine particle sulfur concentrations than to ozone formation. Local scale primary emissions also contribute to the ambient fine particle sulfur concentrations at core urban locations.

Key word index: St. Louis, MO, ozone, sulphate, photochemical, urban plume.

A number of investigations have been published on relationships involving particulate sulfate over regions of North America (Altshuller, 1976, 1980; Hidy *et al.*, 1978; Whelpdale, 1978; Wolff *et al.*, 1979). Elevated concentrations of sulfate and ozone have been identified as occurring during the same periods in the summer months of the year in the United States (Altshuller, 1980; Ferman *et al.*, 1981; Hidy *et al.*, 1978; Husar *et al.*, 1976; Lioy *et al.*, 1977, 1980; Parekh and Husain, 1981; Wolff *et al.*, 1979).

Particle sulfur and particle mass measurements obtained from a number of the regional monitoring stations (RAMS) in and around St. Louis, MO during the Regional Air Pollution Study (RAPS) have been discussed previously (Alpert and Hopke, 1981; Altshuller, 1982; Dzubay, 1980; Loo *et al.*, 1978; Trijonis *et al.*, 1980). Ozone measurements made in the RAPS study have received separate consideration (Karl, 1978a,b; Shreffler and Evans, 1982).

The large extended series of concurrent measurements of fine particle sulfur, fine particle mass and ozone at both urban and nonurban locations in the St. Louis area provides an opportunity to examine relationships among these species in detail. The emphasis in this work will be on the patterns of concentration of these species particularly during periods of especially high concentrations, episodic periods.

PROCEDURE

Samples of particulate matter were collected by the use of dichotomous samplers at ten of the regional air monitoring stations, (RAMS) in the St. Louis area. These stations were designated as RAMS 103, 105, 106, 108, 112, 115, 118, 120, 122 and 124. The geographical locations of these stations are shown in Fig. 1 and the character of these locations are briefly presented in Table 1. This sampling network was one component of the ground and aircraft based measurement system of the Regional Air Pollution Study (RAPS).

The dichotomous samplers separated the particles so as to provide a finer size fraction of less than 2.4 μm and a coarser

Table 1. Brief descriptions of the aerosol sampling locations in the RAPS network

Station	Local environment
103	National City, Illinois. Amidst heavy industries, railroad, army depot and vehicular traffic. Open area 0.5 km around site. Power plant 2.2 km to the NW.
105	South central St. Louis. Among trucking and warehousing operations. Close to chemical plants. Heavy industry 3 km to the E.
108	6 km NW of Granite City, Illinois, among farmland. Steel operations 4.5 km to the SE. Cement plant 5.8 km to the W.
112	On the athletic field of Washington University. Highway 2 km to the S.
115	23 km NE of St. Louis. Agricultural area. Petrochemical plant 5.8 km to the NW.
118	16 km S of St. Louis on farmland. Petrochemical plants 7 km to the NE.
120	24.5 km W of St. Louis. Light industrial park. Heavy traffic 1.8 km to W and 0.2 km to the S.
122	45 km N of St. Louis. Agricultural area. No major pollution source nearby.

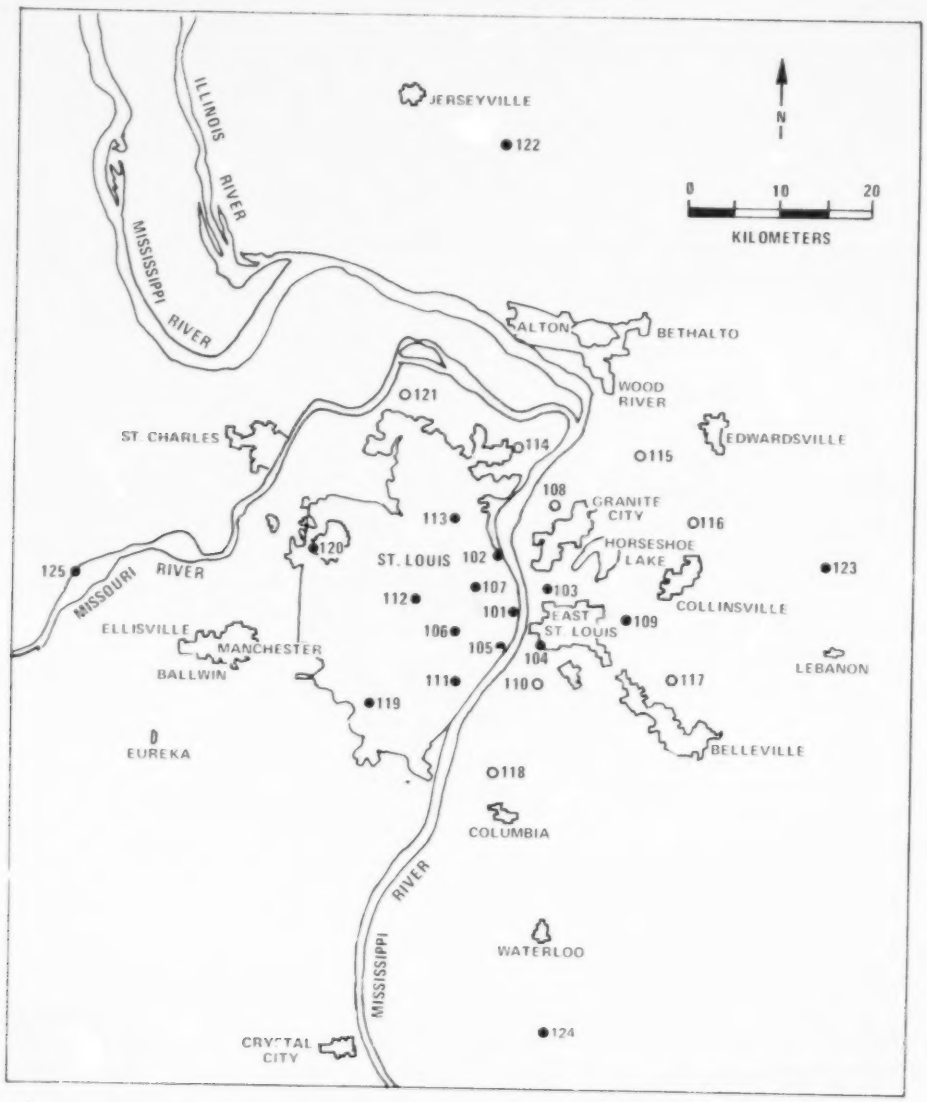

Fig. 1. The St. Louis region, rivers and RAMS sites. Solid dots indicate 30-m towers, and open circles indicate 10-m towers.

size fraction between 2.4 and 20 μm. In this work the emphasis will be on the measurements made on the finer size fraction. The sampling procedures and the analytical methodologies have been reported previously (Altshuller, 1982; Dzubay and Stevens, 1975; Dzubay *et al.*, 1977; Goulding *et al.*, 1975; Jaklevic *et al.*, 1977; Loo *et al.*, 1976, 1978; Stevens *et al.*, 1978). These measurements provided both particle mass and the chemical composition of the two size fractions.

The sampling intervals for collection of the particulate matter varied among stations and with time period. Six hour average samples usually were collected at stations 103 and 105 from 0000 to 0600 h, 0600 to 1200 h, 1200 to 1800 h and 1800 to 2400 h from June 1975 to March 1977. At the eight other stations sampling began in either May or June 1975 and continued until the summer of 1976 at stations 106 and 124 and either to the end of December 1976 or January 1977 at the other six stations. Twelve hour average samples usually were collected. However, 6-h average samples were collected for somewhat varying time periods in July–August 1975 at these stations. At stations 108 and 115 6-h average samples also were collected from late July or the beginning of August to the beginning of September 1976. Two-hour average samples were collected for a period of about a month in July into August 1975 at stations 103, 105 and 112.

Records of ozone measurements are available at all twenty five of the RAMS stations from the beginning of 1976 through the first half of 1977. Shreffler and Evans (1982) have presented the time series by day for the years 1975 and 1976. The peak 1-h average ozone concentrations and the 1200–1500-h average upwind inflow ozone concentrations are available in printouts along with average temperatures, solar radiation, wind speeds and direction.

In some of the results to be presented, particle sulfur will be expressed in terms of its molecular composition.

Measurements of strong acidity and the composition of sulfates are available by several techniques in the St. Louis area (Charlson *et al.*, 1974, 1978; Cobourn *et al.*, 1978; Cobourn and Husar, 1982) and in other urban areas (Leaderer *et al.*, 1982; Tanner, pers. comm., 1983; Tanner *et al.*, 1979) and nonurban areas (Ferek *et al.*, 1983; Ferman *et al.*, 1981; Kumar *et al.*, 1982; Leaderer *et al.*, 1982; Pierson *et al.*, 1980; Stevens, pers. comm., 1983; Stevens *et al.*, 1978, 1980; Tanner, pers. comm., 1983; Tanner and Marlow, 1977; Weiss *et al.*, 1982) in the eastern United States. These measurements of acidities indicate compositions usually corresponding to either $(NH_4)_2SO_4$ or within the range of $(NH_4)_2SO_4$ and $(NH_4)_3H(SO_4)_2$ for urban areas. Within lower elevation nonurban areas, the compositions usually are in the range between $(NH_4)_2SO_4$ and $(NH_4)_3H(SO_4)_2$. An average composition corresponding to $(NH_4)_3H(SO_4)_2$ was selected to use for the results on particle sulfur obtained within St. Louis and adjacent nonurban locations.

RESULTS

Distribution of elevated fine particle sulfur and particle mass concentrations with season of the year

The distribution of elevated concentrations of fine particle sulfur and particle mass with seasons of the year was of interest. To examine such distributions it was decided to use the subset of samples containing concentrations of fine particle sulfur and particle mass in the 95th percentile and above. The distributions of samples by month of the year in the 95th percentile and above were calculated from the measurements at seven of the RAMS stations, 103, 105, 108, 112, 118, 120 and 122 for the year 1976. The percentages of samples with concentrations in the 95th percentile and above by month of the year 1976 for fine particle sulfur, fine particle mass and coarse particle mass are shown in Fig. 2. Most samples containing concentrations of fine particle sulfur and of fine particle mass in the 95th percentile and above were collected during the late spring and summer months. However, samples containing concentrations of coarse particle mass in the 95th percentile and above were more uniformly distributed within many more samples collected in the cooler months of the year.

The concentration distributions of fine particle sulfur and fine particle mass also were examined for the months in 1975 and 1977 when measurements were available. The same 95th percentile values were used for these months in 1975 and 1977 as obtained for all of 1976. Based on this selection of values, very small numbers of samples containing such elevated concentrations of fine particle sulfur and of fine particle mass were collected either during the 4th quarter of 1975 or the 1st quarter of 1977. As for 1976, most of the elevated concentrations of fine particle sulfur and of fine particle mass were collected in June through August. A difference observed between the June–August periods of these two years was the much larger number of elevated concentrations of fine particle sulfur and fine particle mass during the month of July in 1975.

Episodic periods of elevated concentrations of fine particle sulfur and fine particle mass

Substantial clustering of samples with concentrations of fine particle sulfur and of fine particle mass in the 95th percentile and above occur even within

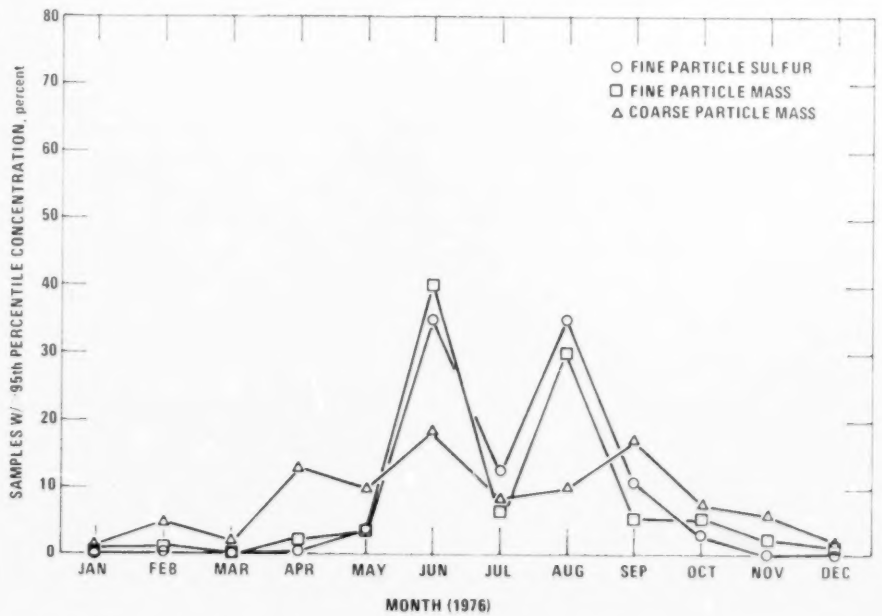

Fig. 2. Percentage of samples containing concentrations of fine particle sulfur, fine particle mass and coarse particle mass in the 95th percentile and above by month of the year 1976 at RAMS stations in the St. Louis area.

the June to August periods. For example, during 1976 three-quarters of the samples of fine particle sulfur and two-thirds of the samples of fine particle mass with concentrations in the 95th percentile and above were collected during two periods. These periods included (1) the first half of June (2) from the middle of August to the first few days in September. Similar lengths of such episodic periods occur in 1975. Such periods will be referred to subsequently as episodic periods.

Daily variations in 12-h average fine particle sulfur concentrations from just before to immediately after one episodic period in 1975 and in 1976 are shown in Figs 3 and 4. Very substantial increases in fine particle sulfur concentrations occur at the beginning of such episodic periods followed by large decreases in fine particle sulfur concentrations at the end of each period. Within each episodic period substantial day-to-day variations in fine particle sulfur concentrations also often occur.

In Table 2 the fine particle sulfur concentrations are given for 14 representative episodic days in 1975 and 1976. Fine particle sulfur concentrations are listed same 6 or 12-h average time period at the core urban stations 103 and 105, at upwind stations in the inflow of air from adjacent nonurban areas and for stations in the air flow downwind of St. Louis. Examples of stations in the inflow (I) or downwind (D) also are given for several days in Figs 3 and 4. The concentration values given for the inflow and downwind do not necessarily represent the changes occurring with movements of a given set of air parcels.

Based on the results given in Table 2 the fine particle sulfur concentrations at the stations in the inflow air range from 34 to 95% and average 73% of the concentrations at core urban stations during the same period of each of the days. Similarly, the fine particle sulfur concentrations at stations downwind of St. Louis range from 102 to 184% and average 142% of the concentrations at stations upwind in the inflow air. Therefore, the incremental fine particle sulfur concentrations downwind compared to upwind vary widely from day to day even during episodic periods. Based on results similar to those given in Table 2 but for fine particle mass rather than fine particle sulfur similar results were obtained. The fine particle mass concentrations at the stations in the inflow air average 63% of the concentrations at the core urban stations. The fine particle mass concentrations at stations downwind of St. Louis average 121% of the concentrations at stations upwind in the inflow air.

The concentrations of fine particle sulfur and of fine particle mass tend to increase and decrease together through episodic periods based on a number of plots prepared for a number of RAMS stations during several of the episodic periods. However, it also was noted that there was not an exact proportionality between the fine particle sulfur and fine particle mass concentrations. There was a range of variability from sample to sample. Superimposed on such variations was the tendency at high particle sulfur concentrations for the increase in the fine particle mass concentration to lag behind the increase in fine particle sulfur. Such behavior is illustrated in Fig. 5. In this figure, the percentage of fine particle sulfur, expressed as having the composition $(NH_4)_3H(SO_4)_2$, in the fine particle mass is plotted vs fine particle sulfur. The percentage of the fine particle mass accounted for as $(NH_4)_3H(SO_4)_2$ clearly increases significantly at the higher particle sulfur concentrations. Similar plots showing the same characteristics were obtained from measurements at other RAMS stations during the same episodic period

Table 2. Particle sulfur concentrations at RAMS stations in urban locations, in inflow air and in downwind flow of St. Louis and associated ozone concentrations

Date	Particle sulfur concentrations* ($\mu g\,m^{-3}$) Urban†	Inflow	Downwind	Ozone concentrations (ppbv) Inflow, 1200–1500 h av.	1-h max.
27.6.75	13.2	8.8‡	16.2‡	81	202
28.6.75	13.8	12.0‡	12.2‡	92	148
2.7.75	13.2	9.8‡	12.9‡	116	209
3.7.75	14.6	13.8‡	23.1‡	116	184
4.7.75	12.4	10.4‡	16.3‡	91	104
16.7.75	6.1	4.9	7.9‡	83	142
17.7.75	7.0	5.6	6.5‡	67	168
9.8.75	17.4	10.9‡	19.7‡	97	166
8.9.75	9.9	3.4	4.5‡	49	255
1.6.76	7.7	4.8	7.7‡	96	151
7.6.76	9.3	6.6	8.8‡	125	198
8.6.76	12.8	8.4	11.1	126	221
11.6.76	6.0	5.4	6.2‡	90	133
23.8.76	13.4	8.8‡	10.3	86	156

*Particle sulfur concentrations tabulated are those corresponding to the same periods of the day during which ozone concentrations reached their maximum values.

†Average of the concentrations of fine particle sulfur measured at RAMS stations 103 and 105.

‡Average of concentrations of fine particle sulfur at the two or three RAMS stations in either the inflow air or downwind flow from St. Louis. If not so footnoted measurements limited to one station.

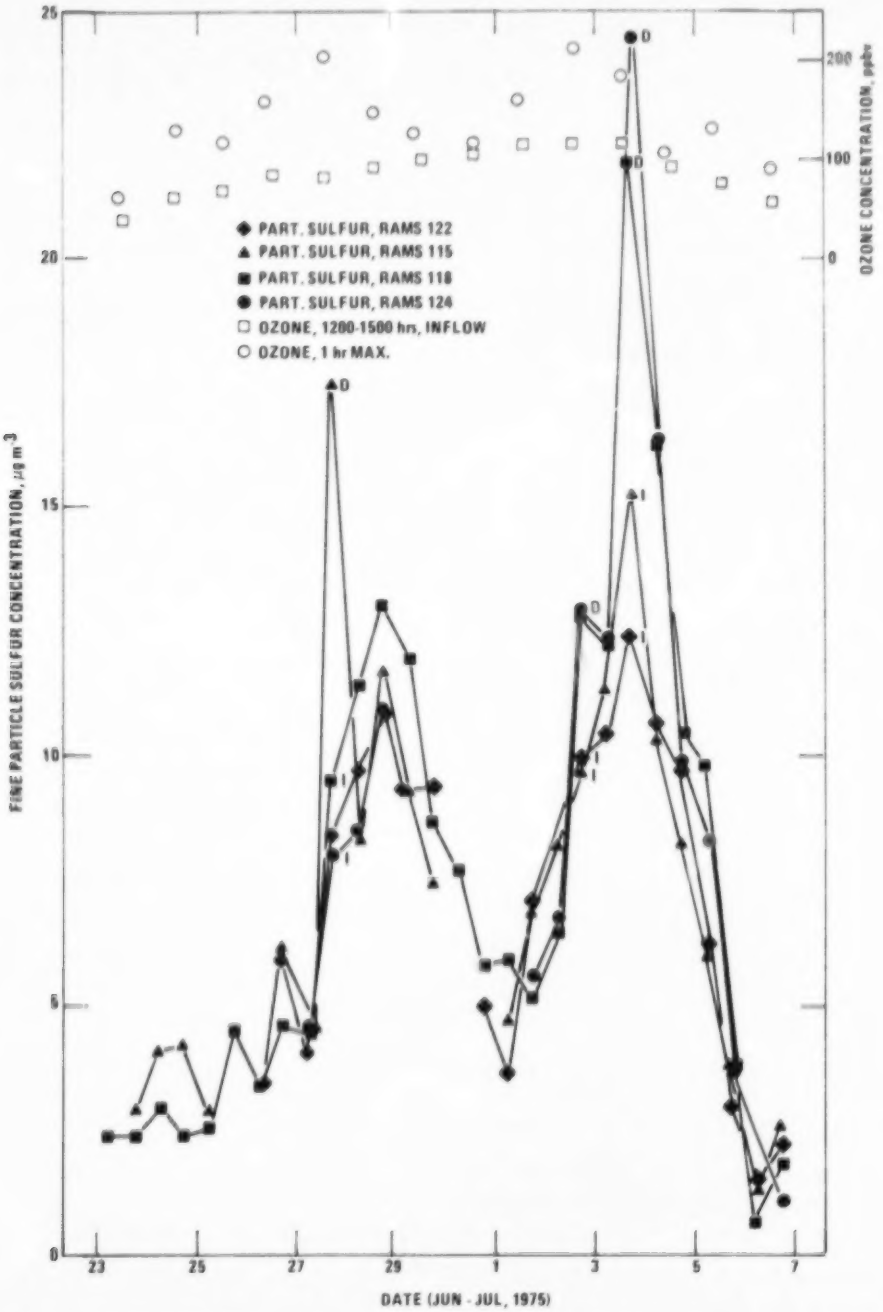

Fig. 3. Day to day variations in the concentrations of fine particle sulfur and of ozone at RAMS stations in St. Louis area before, during and after episodic period in June–July 1975.

in 1976 as well as during other episodic periods.

The concentration differences between the fine particle mass and the fine particle sulfur as $(NH_4)_3H(SO_4)_2$ should represent the concentrations of the sum of other species in the fine particle mass. These differences, the non-sulfur fine particle mass do not increase consistently along with the fine particle sulfur concentration during episodic periods. Intermediate and occasionally low concentrations of non-sulfur fine particle mass occurred in samples

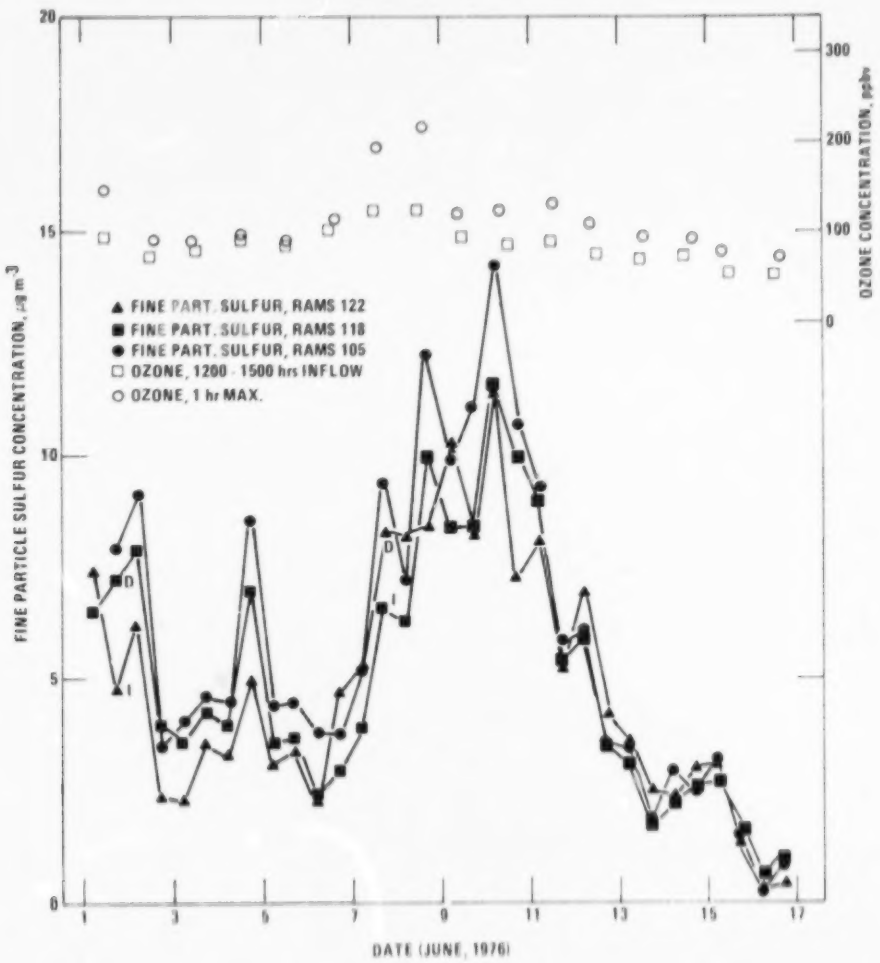
FINE PARTICLE SULFUR CONCENTRATION, μg m⁻³
OZONE CONCENTRATION, ppbv
DATE (JUNE, 1976)
▲ FINE PART. SULFUR, RAMS 122
■ FINE PART. SULFUR, RAMS 118
● FINE PART. SULFUR, RAMS 105
□ OZONE, 1200 - 1500 hrs INFLOW
○ OZONE, 1 hr MAX.
D
I

Fig. 4. Day to day variations in the concentrations of fine particle sulfur and of ozone at RAMS stations in St. Louis area before, during and after episodic period in June 1976.

containing high concentrations of fine particle sulfur.

For the same group of days considered in Table 2 the non-sulfur fine particle mass concentrations at stations in the inflow air averaged 48 % of the concentrations at the core urban stations 103 and 105. The non-sulfur fine particle mass concentrations downwind compared to those at stations in the inflow air showed no consistent patterns. No clear indications of incremental non-sulfur fine particle mass concentrations downwind was evident as was observed for fine particle sulfur.

Variations in fine particle sulfur and of ozone concentrations during episodic periods

It is of interest to relate fine particle sulfur concentrations to ozone concentrations during episodic periods. Time series for the surface ozone concentrations measured at the RAMS stations in the St. Louis area are available for 1975 and 1976 (Shreffler and Evans, 1982).

The maximum 1-h ozone concentration measured at any station within the RAMS network was obtained for each day in 1975 and 1976. In addition, the daily average inflow ozone concentration was calculated for the 1200–1500 h CST period using the ozone measurements available at the three upwind nonurban RAMS stations in the outer ring of stations. These inflow ozone concentrations were considered representative of regional scale characteristics and to vary with passage of large scale weather systems (Shreffler and Evans, 1982).

For the 49 days during 1976 when the fine particle sulfur concentrations were in the 95th percentile and above at one or more of the RAMS stations, the 1-h maximum ozone concentrations exceeded 120 ppbv on 34 of these days (69 %) and exceeded 80 ppbv on 46 of these days (94 %). The inflow ozone concentrations exceeded 80 ppbv on 32 of these 49 days (65 %). Conversely, on the 33 days in 1976 when the maximum

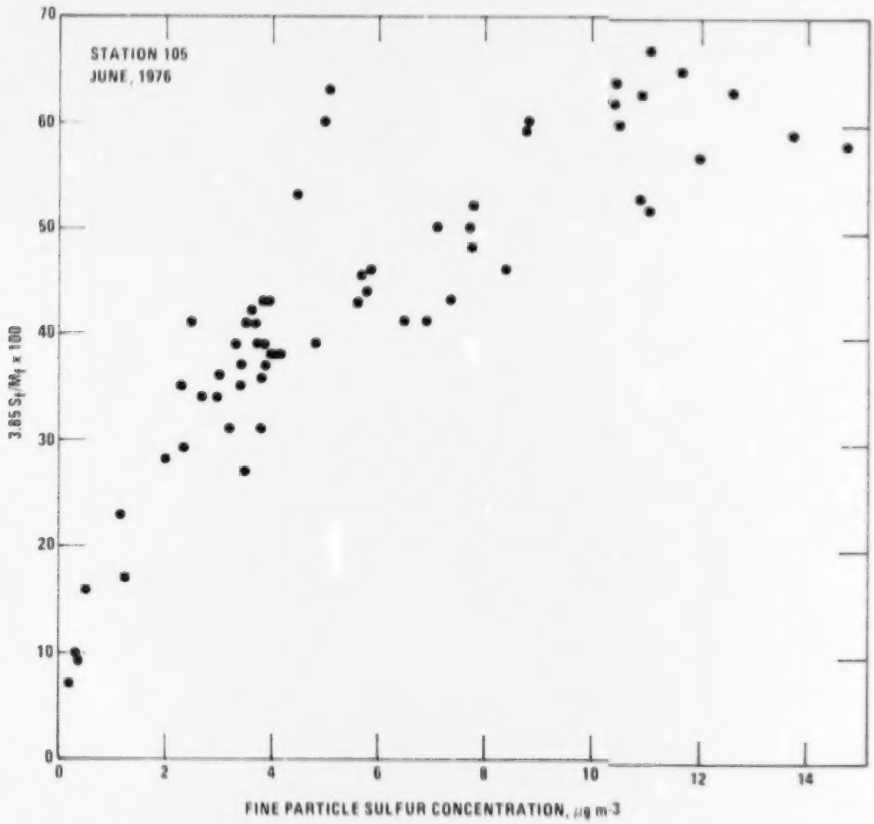

Fig. 5. Percentages of fine particle sulfur in fine particle mass with variations in fine particle sulfur concentrations during June 1976 at RAMS station 105.

1-h ozone exceeded 120 ppbv and the inflow ozone concentration exceeded 80 ppbv, the fine particle sulfur concentrations were in the 95th percentile and above on 27 of these days (82%) and were in the 85th percentile and above on 31 of these days (94%). Therefore, there was a strong qualitative association between high fine particle sulfur concentrations and elevated ozone concentrations.

The relationships between fine particle sulfur concentrations and ozone concentrations also are illustrated in Figs 3 and 4. Both the fine particle sulfur concentrations at several RAMS stations and the maximum 1-h ozone concentrations and average daily 1200–1500 h CST inflow concentrations are plotted concurrently. The fine particle sulfur concentrations listed are for the same 6- or 12-h time interval within the maximum 1-h O_3 concentration occurs. Based on these plots as well as comparisons made during other episodic periods, it is observed that fine particle sulfur and ozone frequently tend to peak on the same day during episodic periods, but exceptions are not uncommon.

The peaking in the fine particle sulfur concentrations proceeded or lagged the peaking in the maximum 1-h O_3 concentrations usually by about one day within some episodic periods. The highest percentile 1-h maximum O_3 concentrations also did not occur together with the highest percentile fine particle sulfur concentrations. The increases in fine particle sulfur concentrations within compared to outside of episodic periods usually were greater than were observed for the O_3 concentrations.

The fine particle sulfur concentrations and the O_3 concentrations measured at stations within the inflow air were compared. Measurements obtained between June and September 1975 are used for those days on which the 1-h O_3 maximum concentration exceeded 120 ppbv (Fig. 6). A tendency can be observed for the fine particle sulfur to increase with increasing inflow O_3 concentrations.

Although 1-h maximum O_3 concentrations above 100 ppbv were not common in the St. Louis area during the early spring and fall months, such concentrations were measured on a number of such days in 1975 and 1976. The fine particle sulfur concentrations were low on all of these days at stations in the inflow air

as well as at non-urban stations downwind. Elevated fine particle sulfur concentrations were measured on a few of these days at core urban stations.

DISCUSSION

The observation during episodic periods of elevated sulfur concentrations concurrently measured along with elevated ozone concentrations indicates an association which can be attributed to similar processes of formation. Such an association is consistent with what is known about the atmospheric formation mechanisms for conversion of SO_2 to fine particle sulfur. The homogeneous gas phase reactions of SO_2 to form fine particle sulfur depend on the availability of free radical species formed by the same reaction sequences producing O_3, while the reactions in droplets leading to sulfate formation involve oxidation of SO_2 by atmospheric oxidants, H_2O_2 and O_3 (Miller *et al.*, 1983).

However, there also are a number of differences in the atmospheric characteristics of O_3 and fine particle sulfur as well as experimental limitations which must be considered.

(1) Ozone unlike particle sulfur can be consumed by atmospheric reactions particularly those with nitric oxide. This reaction is particularly significant in limiting O_3 concentrations near the surface at night and in the morning hours. The diurnal O_3 profiles in St. Louis (Karl, 1978b) as in other cities are consistent with this consumption process.

(2) In the rural locations O_3 would be depleted at night primarily by dry deposition, since nitric oxide concentrations are negligible. The rural diurnal profiles show such depletion (Karl, 1978b). Available diurnal profiles for fine particle sulfur in St. Louis (Figs 3 and 4) and elsewhere (Stensland *et al.*, 1983) are not similar to those for O_3.

(3) There is a large reservoir of O_3 in the free troposphere (Fishman and Seiler, 1983), whereas there is a very low background concentration of fine particle sulfur in the free troposphere (Rodhe and Isaken, 1980).

(4) Despite all of these differences between O_3 and fine particle sulfur a number of relationships do exist between the two species. An experimental limitation is imposed by the samples for particle sulfur being collected over 6- or 12-h periods while O_3 is measured continuously. Among other problems, this mismatch in sampling periods makes it more difficult to define air parcel trajectories across the urban area to downwind locations.

As demonstrated by the results presented earlier (Table 2), substantial concentrations of fine particle sulfur occur during episodic periods in the inflow of air from nonurban areas upwind. These inflow concentrations are a large fraction of the fine particle concentrations measured in core urban areas.

As illustrated in Fig. 6, the variations in the fine particle sulfur in the inflow air follow those of O_3 in the inflow air (correlation coefficient, 0.81). A review of the background of particle sulfur in the continental and maritime boundary layer and free troposphere indicates background concentrations at or below 0.1–0.2 $\mu g\,m^{-3}$ (Altshuller, 1983; Rodhe and Isaksen, 1980). The value of about 45 ppbv for O_3 corresponding to this background particle sulfur concentration in Fig. 6 is consistent with the lower tropospheric background for O_3. (Fishman and Seiler, 1983). The increments above this background shown by both species suggest that the incremental formation of these species is associated with similar regional scale processes within the boundary layer. In particular, the concurrent elevation in the concentrations of both species in the inflow during the same days in the late spring and summer also generally involving high ambient temperatures and light intensities and the passage of high pressure systems is consistent with their formation by regional scale atmospheric photochemical processes.

Substantial incremental fine particle sulfur concentrations are observed on a number of days downwind of St. Louis relative to the concentrations at upwind inflow locations (Table 2). These incremental concentrations of fine particle sulfur across the urban area occurred on days characterized by high 1-h maximum O_3 concentrations as well as high inflow O_3 concentrations. In addition, on these days the average wind speeds (0700–1359 CST) usually were low, less than 2 $m\,s^{-1}$. These combinations of circumstances suggest the following scenario. The accumulating urban emissions of hydrocarbons and nitrogen oxides react to form free radical intermediates such as hydroxyl radicals. Because of the slow movement of the air parcels across the urban/industrial areas of the city, sufficient reaction time is available for the free radicals to react with and convert an appreciable fraction of the accumulating urban emissions of SO_2 to fine particle sulfur. As a result, variable increments of fine particle sulfur are transported to RAMS stations downwind of the city compared to the fine particle sulfur in the inflow air. Variable rates of conversion of SO_2 have been observed in other urban plumes even on consecutive days with very similar meteorological conditions (Miller *et al.*, 1983).

Other shorter intentive studies in the St. Louis area provide evidence for transport and formation of particle sulfur, in the St. Louis urban plume well beyond the outermost ring of RAMS stations (Ellestad, 1980; Rasmussen *et al.*, 1977). Measurements of particle sulfur, O_3 and other gaseous and aerosol species were obtained at a rural location 104 km north-northwest of the St. Louis Arch during the latter half of July and first part of August 1975. During four time periods of 8 and 9 August 1975 the increases in concentrations of several urban pollutant species along with air trajectory analyses indicated that the site was within the St. Louis plume. During these periods the particle sulfur concentrations peaked at 5, 6, 8 and 15 $\mu g\,m^{-3}$. The O_3 concentrations at this site during

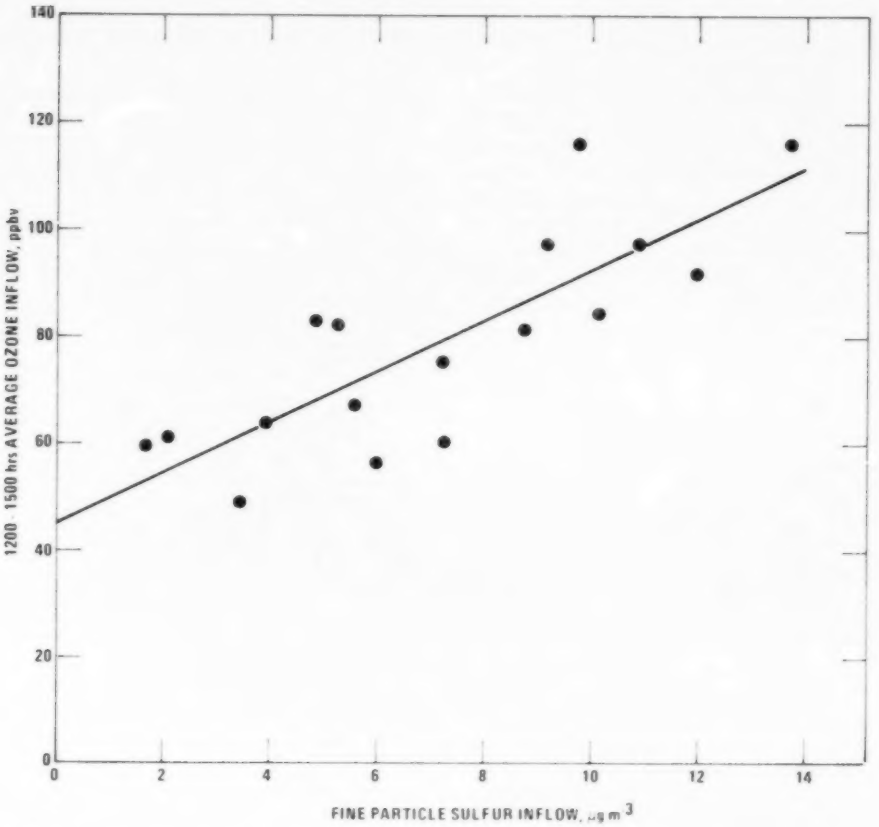

Fig. 6. Scatter plot of inflow fine particle sulfur concentrations and inflow O_3 concentrations (1200–1500 CST).

the evening hours reached 130 ppbv on 8 August and 92 ppbv on 9 August. In an aircraft tracking of the St. Louis plume over an 18-h period on 28 and 29 July 1975, the particle sulfur was shown to increase in concentration downwind of St. Louis and peak at 20 $\mu g\ m^{-3}$ between 70 and 110 km downwind (Wilson, 1978).

On yet other days when the 1-h maximum O_3 concentrations observed within or downwind of St. Louis were well above the O_3 concentrations in the inflow air, significant increments of fine particle sulfur did not occur in downwind air compared to inflow air. Nevertheless, on these days the fine particle sulfur concentrations at core urban stations were elevated well above the concentrations in the inflow air. While these circumstances were observed on some days during the summer, they also occurred during a few days in late September and early October with high 1-h maximum O_3 concentrations. The lack of incremental fine particle sulfur concentrations downwind indicates that conditions were not favorable to appreciable rates of photochemical formation of fine particle sulfur occurring in the St. Louis area. Free radical concentrations have been estimated to decrease substantially from summer to fall months at the latitude of St. Louis (Altshuller, 1979). Therefore, elevated fine particle sulfur concentrations measured at core urban stations under these circumstances appear likely to be associated with local emissions of primary fine particle sulfur.

Comparison of the ratios of downwind to inflow concentrations of fine particle sulfur and of O_3 as in Table 2 indicated on average a somewhat larger portion of the fine particle sulfur downwind is likely to be associated with regional scale boundary layer processes than is so for O_3. However, on those individual days with large urban increments of fine particle sulfur the ratios did become comparable for fine particle sulfur and for O_3.

The discussion above is consistent with the presence of elevated concentrations of fine particle sulfur along with elevated concentrations of O_3 in the St. Louis area involving several different processes. These processes are as follows: (1) regional scale atmospheric photochemical formation of fine particle sulfur and O_3 with transport into the area by high velocity nocturnal winds aloft (Evans, 1979). These species are transported down to surface locations by (1) vertical mixing

during the daylight hours, (2) local photochemical formation of fine particle sulfur along with O_3 during the day as air parcels are transported slowly across the urban area to downwind nonurban locations and (3) local scale primary emissions of fine particle sulfur. The relative contributions of these several processes to fine particle sulfur formation varies from day to day even when the O_3 concentrations were elevated on all days under consideration. These results indicate that urban plume models (Balko and Peters, 1983; Gillani *et al.*, 1983; Isaksen *et al.*, 1978) attempting to predict SO_2 transformations to particle sulfur which do not consider the details of air parcel movements across urban, industrial/suburban areas of cities are unlikely to be able to accurately predict day-to-day variations in the accumulation of particle sulfur downwind.

Earlier it was noted that the peaking in fine particle sulfur during an episodic period may either lead or lag the peaking in the O_3 concentration. One possible explanation for lagging of the fine particle sulfur concentrations during episodes would be the relatively slow rate of conversion of SO_2 to fine particle sulfur often observed even within plumes (Miller *et al.*, 1983). Since the fine particle sulfur is not depleted substantially at night and can build up day by day, the fine particle sulfur would continue to increase in concentration and could peak somewhat later in an episode. Again it should be emphasized that whether an episode occurred near the summer solstice or significantly earlier or later can effect the rate of homogeneous formation of particle sulfur substantially (Altshuller, 1979).

The lead or lag effect on peaking of various species may result from the influence of larger scale meteorological movement on these species. Husar and coworkers (1976) discussed the episode of late June and early July 1975 (Fig. 3) as air masses moved back and forth across the eastern United States. These investigators used ozone measurements for O_3 at 89 sites and visibility measurements at several hundred sites to construct O_3 and visibility isopleths every other day from 25 June to 5 July for the eastern United States. In addition, isopleths for sulfate were constructed from measurements at about 60 sites on 23 June and 5 July 1975.

The visibility started to deteriorate on 25 June in the midwestern United States and continued to do so for the next several days. By 29 June, the visibility was greatly reduced in a midwestern region including the St. Louis area, but by 1 July the zone of poorest visibility had moved west of St. Louis. Subsequently, the movement of the air mass became easterly resulting in the visibility in St. Louis becoming very poor again on 3 July, but improving substantially by 5 July.

On 23 June and 5 July 1975 when both visibility and sulfate isopleths were available, a good coincidence of isopleths of reduced visibility and elevated sulfate concentrations was obtained. A number of subsequent studies in the eastern United States support a high correlation between light extinction coefficients and fine particle mass with a large part of the light extinction being accounted for by the particle sulfur present (Altshuller, 1983).

At the RAMS stations in the St. Louis area (Fig. 3) the particle sulfur concentrations plotted show a similar sequence of variations as does the visibility with particle sulfur concentrations increasing from 25 June to 28 and 29 June, decreasing on 30 June and 1 July and increasing again on 3 and 4 July only to decrease rapidly in concentration by 5 July.

In comparison with the changes in visibility, O_3 concentrations built up to high levels by 27 June, but the O_3 concentrations did not decrease as drastically as the visibility improved by 1 July nor did the O_3 concentrations decrease as rapidly as the visibility improved near the end of the episode (Husar *et al.*, 1976). The O_3 concentration changes in the St. Louis (Fig. 3) are in good agreement with those observed regionally. Therefore, it appears likely that the peaking of the O_3 relative to particle sulfur in this episode and probably in certain other episodes can relate to such larger scale regional air mass movements.

As mentioned earlier, fine particle mass and particularly the sum of non-sulfur particle mass concentrations do not tend to track fine particle sulfur concentrations during episodic periods. Similarly, the sum of non-sulfur fine particle mass concentrations do not follow the variations in O_3 concentrations either. Non-sulfur particle mass concentrations tend to be much higher at core urban stations than at either inflow and downwind stations. Furthermore, no consistent concurrent formation of incremental non-sulfur fine particle mass was measured along with fine particle sulfur at downwind stations. All of these observations are consistent with different processes being responsible for the presence of the non-sulfur components of fine particle mass than for the fine particle sulfur. If other photochemically produced non-sulfur aerosol species such as certain types of organic aerosols and nitrate aerosols constituted a major part of the non-sulfur fine particle mass, the non-sulfur fine particle mass concentrations might be expected to follow the variations in fine sulfur concentrations reasonably closely. The fact that such relationships do not occur suggest that the non-sulfur fine particle mass may be contributed to largely by primary local scale particulate emissions within the urban area of St. Louis.

CONCLUSIONS

(1) Substantially elevated concentrations of fine particle sulfur and fine particle mass tend to be clustered into several time periods in the months of June–August 1975 and 1976 in the St. Louis area.

(2) During time periods when fine particle sulfur concentrations are particularly high, fine particle sulfur constitutes an especially large percentage of the fine particle mass measured.

(3) The sum of the non-sulfur fine particle mass species do not increase along with fine particle sulfur during late spring and summer months.

(4) Elevated concentrations of fine particle sulfur and of O_3 tend to occur together during the same episodic periods.

(5) On individual days during episodic periods with high 1-h maximum concentrations of O_3 inflow fine particle sulfur increases along with inflow O_3.

(6) At very low background inflow fine particle sulfur concentrations, inflow ozone, 1200–1500 CST, was present at about 45 ppbv.

(7) Averaging over a group of days during episodic periods of elevated fine particle sulfur concentrations, inflow fine particle sulfur constituted slightly over 70% of the fine particle sulfur measured at core urban locations.

(8) Incremental fine particle sulfur concentrations at downwind locations substantially above those at inflow locations were measured on a number of episodic days. These days usually were characterized by low wind speeds below 2 $m\,s^{-1}$ as well as high temperature and solar intensities along with O_3 concentrations above 120 ppbv.

(9) Other measurements at ground level and in aircraft of air parcels transported well beyond the outermost circle of RAMS stations in St. Louis provide evidence on several days for transport of high incremental concentrations of particle sulfur at least 100 km downwind of St. Louis.

(10) On some days when incremental fine particle sulfur was not observed downwind, fine particle sulfur concentrations still were elevated at core urban locations. These elevated concentrations can be attributed to local primary fine particle sulfur emissions.

(11) The leading or lagging of peak O_3 compared to peak particle sulfur concentrations during one episodic period were shown to relate well to larger scale meteorological movements in the eastern United States.

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